

Self-discharge of carbon-based supercapacitors with organic electrolytes

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Abstract

The self-discharge behaviour of supercapacitors is an important factor when considering their suitability for some applications. In this paper, measurements of the self-discharge rates of carbon-based supercapacitors with organic electrolytes are presented and interpreted in terms of two mechanisms. The first is the diffusion of ions from regions of excess ionic concentration formed during the charging of the capacitor and the second is leakage of charge across the double-layer at the electrolyte–carbon interfaces in the capacitor. The dependence of the self-discharge rate on temperature and on the initial voltage across the capacitor is described. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Supercapacitors; Self-discharge rate; Electrolyte–carbon interfaces

1. Introduction

Supercapacitors are used for storing energy over time periods ranging from seconds to several days. The main factor determining the energy storage time of a supercapacitor is its self-discharge rate. Self-discharge of a supercapacitor refers to the gradual decrease in the voltage across the capacitor that occurs when the capacitor is left unconnected to either a charging circuit or an electrical load. In chemical cells, the self-discharge rate is very slow and the shelf-life is measured in many months, if not years. From the beginning of the development of supercapacitors, it has been found that they have much higher self-discharge rates than chemical cells and at their present state of development they cannot be marketed as a component in a charged state.

All capacitors slowly lose their charge and, hence, their stored energy. In conventional capacitors (plastic film, electrolytic, etc.), the self-discharge process can be adequately modelled by representing the capacitor as a capacitance C in parallel with a constant leakage resistance R_{le} . In this case, the voltage V at time t is given by:

$$V = V_0 e^{-t/R_{le}C} \quad (1)$$

where V_0 is the initial voltage across the capacitor and t is the time elapsed since the commencement of self-dis-

charge. This paper describes the mechanisms which result in carbon-based supercapacitors with organic electrolytes having a self-discharge behaviour that cannot be adequately represented by Eq. (1). We illustrate the self-discharge behaviour with details of measurements made with the prototype supercapacitor SCA272. Aspects of the self-discharge behaviour of seven other supercapacitors are presented in Table 1 in Section 3 of the paper.

2. Measurements of self-discharge in a prototype supercapacitor

The prototype supercapacitor SCA272 used for the measurements reported here has a capacitance of approximately 26 F and an equivalent series resistance (esr) of 0.06 Ω . The capacitor is of spiral-wound construction with electrodes which consist of carbon adhered to aluminium foil. The electrolyte is tetraethylammonium tetrafluoroborate with propylene carbonate as the solvent.

Capacitor SCA272 was charged with a constant-voltage supply for about 1 h and then allowed to undergo self-discharge for 16 h. After this long charging time, all of the capacitive elements of the capacitor would have been charged to approximately the same voltage. Consequently, when the charging current had stopped, the capacitor voltage did not decrease rapidly due to the effects of redistribution of charge among the capacitive elements. When

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Table 1
Values of diffusion parameter m for eight capacitors

Capacitor	Initial voltage	C (F)	Electrolyte	Diffusion parameter m (mV/s ^{1/2})
SCA182	2.1	13.7	TEATFB in PC	3.6
SCA244	2.0	13.6	TEATFB in PC/7P01	3.5
SCA245	1.87	12.5	TEATFB in PC/7P01	19
SCA272	2.4	26	TEATFB in PC	5.3
SCA274	1.85	93	TEATFB in PC	2.8
SCA290	2.3	41	TEATFB in PC	3
29	2.2	852	TEATFB in PC	5.3
42	2.2	815	TEATFB in PC	6.7

present, such rapid voltage decreases typically occur with time constants of several minutes.

The self-discharge voltages for three initial voltages of 1.55, 2.0 and 2.4 V are shown in Fig. 1. The quite rapid decrease in voltage for a 2.4 V initial voltage represents a considerable loss of efficiency for the capacitor as an energy-storage device. If it is assumed that energy cannot be conveniently extracted from the capacitor at voltages of less than 0.75 V, the energy which is dissipated in self-discharge mechanisms in the first 2 h of self-discharge is 36% of the energy available upon the commencement of self-discharge. Unless the mechanisms of self-discharge can be understood and moderated, supercapacitors of this type may be limited in their ability to store energy efficiently for more than about 30 min.

3. Self-discharge mechanisms

When the measurements in Fig. 1 are plotted as $\ln V$ vs. time (t) it is seen that the self-discharge rates from the

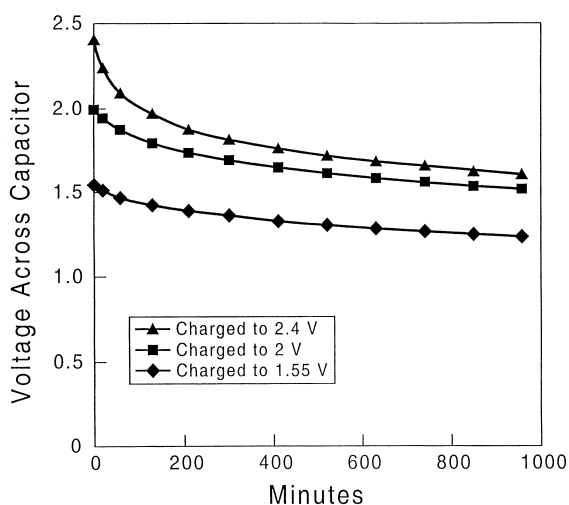


Fig. 1. Voltages during self-discharge of capacitor SCA272 following constant-voltage charging to 3 V.

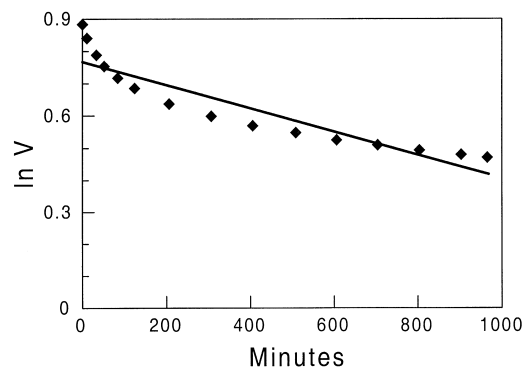


Fig. 2. Self-discharge of capacitor SCA272 after constant-voltage charging to 2.4 V. It is seen that there is only a poor fit to an exponential decay of voltage V across the capacitor.

three initial voltages are not exponential. This is shown in Fig. 2 for self-discharge of capacitor SCA272 from an initial voltage of 2.4 V. The self-discharge rates cannot, therefore, be wholly ascribed to a leakage current through a path of fixed resistance. It is necessary to investigate whether an additional self-discharge mechanism can provide an explanation for the observed behaviour.

One such mechanism [2] which should be considered involves Faradaic processes that can occur when the voltage across an electrolyte–carbon interface exceeds the decomposition potential limit of the electrolyte. Self-discharge by this mechanism should lead to a linear dependence of the capacitor voltage on $\ln t$. The initial voltages in Fig. 1 are well below the potential limit and when the voltages in Fig. 1 are plotted against $\ln t$, a linear fit is not obtained. It remains then to investigate whether diffusion of ionic concentrations can contribute to the observed self-discharge behaviour.

Here, we describe the self-discharge of the capacitor SCA272 in terms of two mechanisms.

(1) A diffusion process which appears to dominate the self-discharge in the first 8 h, or so. Some ionic species in the electrolyte can undergo Faradaic redox reactions, building up a concentration of an ionic species in the electrolyte near the carbon surfaces during charging of the capacitor.

(2) Current leakage through the double-layer at the electrolyte–carbon interface. The current leakage can be modelled by a leakage resistance R_{le} in parallel with the capacitance of the double-layer.

3.1. Equilibration of excess ionic concentration

When a carbon-based supercapacitor is being charged, at least two processes occur near the surface of the carbon. The first process is an increase in the number of ions forming the double-layer at the carbon surface. It is expected that this number will be approximately proportional to the voltage across the double-layer, though in general, a

double-layer will be present at the electrolyte–carbon interface even when the capacitor is in an uncharged state. The second process is a local increase in ionic concentration, at or near the carbon surface, that is not directly related to the double-layer. It might be expected that accumulation of an excess ionic concentration would only occur when a current is flowing through the capacitor and when the voltage across the capacitor is above some threshold value. When the capacitor is disconnected from the charging circuit and allowed to undergo self-discharge, then, apart from charge leakage due to imperfections and impurities in the double-layer, the double-layer charge will stay in place but the excess ionic concentration near the carbon surface will diffuse to an equilibrium state. Some of the ions will diffuse into the electrolyte and others will diffuse to the carbon surface where they will reduce the number of excess charges in the carbon and, hence, decrease the open-circuit voltage of the capacitor.

Excess ionic concentrations can be expected to form near both electrodes (carbon surfaces) of a supercapacitor. As pointed out in Refs. [1,2], the ionic species are different at the two electrodes and the self-discharge behaviour of the capacitor is the result of processes occurring at both electrodes. The rate of decrease in voltage across the capacitor during self-discharge is the sum of the rates of decrease of the voltages across the two electrolyte–carbon interfaces in the capacitor. Here, we will ignore this complication and assume that the diffusion process proceeds at the same rate at the two electrodes.

When a concentration gradient of ionic species R occurs in an electrolyte, the rate of change of the concentration c_R at any point is related to the second-order derivative with respect to distance x from the electrolyte–carbon interface by the diffusion equation:

$$\frac{\partial c_R}{\partial t} = D \frac{\partial^2 c_R}{\partial x^2} \quad (2)$$

where D is the diffusion coefficient of the ions in the electrolyte. Eq. 2 does not include any effect that electric fields near the interface may have on the motion of the ions.

It is assumed that at the commencement of the self-discharge process, the initial excess concentration of ionic species R is constant (c_{R0}) over a region of electrolyte of thickness $2h$ immediately adjacent to each electrolyte–carbon interface of the capacitor. For simplicity, it is further assumed that each electrolyte–carbon interface is plane and that diffusion only occurs normal to the interfaces. The time dependence of the concentration of species R at one of the interfaces is given by Crank [3] as:

$$c = \frac{1}{2} c_{R0} \left[\operatorname{erf} \left(\frac{h}{\sqrt{Dt}} \right) \right] \quad (3)$$

The current entering the carbon surface at time t due to diffusion of species R is:

$$i_{\text{diff}} = \frac{q c_{R0}}{2} \sqrt{\frac{D}{\pi t}} \exp \left(\frac{-h^2}{Dt} \right) \quad (4)$$

where q is the charge carried to the carbon surface by each ion.

The current entering the carbon surface causes a rate of change of the voltage (V_1) across the interface 1 given by:

$$C_1 \frac{dV_1}{dt} = -i_{\text{diff}} \quad (5)$$

where C_1 is the capacitance per unit area of interface 1. Assuming that electrically equivalent processes occur at both electrodes of the capacitor, Eq. (5) can be written as

$$C_{12} \frac{dV}{dt} = -i_{\text{diff}} \quad (6)$$

where C_{12} is the series combination of the capacitances at the two interfaces of the capacitor, per unit area of one of the interfaces, and V is the voltage across the capacitor.

Combining Eqs. (4) and (6), it can be shown that V is given by:

$$V = V_0 - \frac{c_{R0} q \sqrt{D}}{C_{12} \sqrt{\pi}} \left[\sqrt{t} \left(1 - \exp \left(\frac{-h^2}{Dt} \right) \right) + h \sqrt{D} \operatorname{erfc} \left(\frac{h}{\sqrt{Dt}} \right) \right] \quad (7)$$

where V_0 is the initial voltage across the capacitor.

The time dependence of the voltage across a 30-F supercapacitor calculated using Eq. (7) is given in Fig. 3(a) and the same voltage plotted against $t^{1/2}$ is given in Fig. 3(b). The parameters chosen for the calculation are $C_{12} = 0.1 \text{ F m}^{-2}$, $h = 60 \text{ }\mu\text{m}$, $D = 4 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$ [4] and $c_{R0} = 1.7 \times 10^{22} \text{ m}^{-3}$. It is assumed that the ionic species R carries a single electronic charge. From Fig. 3(b), it can be seen that for about the first 3 h (i.e., until $t^{1/2} = 104 \text{ s}^{1/2}$) the drop in voltage is closely proportional to the square root of the time elapsed since self-discharge commenced.

The terms in Eq. (7) containing the exponential function and the error function lead to a slower rate of voltage decrease for times greater than about h^2/D than that predicted by a simple $t^{1/2}$ dependence. Without these terms, Eq. (7) predicts an unrealistic rate of self-discharge for times greater than h^2/D .

It should be remembered that Eq. (7) is based on a simple model of the process which occurs in the capacitor. The processes at the surfaces of the pores of activated carbon can only be very approximately represented by semi-infinite diffusion within the electrolyte and the influence of electric fields on the rate of diffusion has not been

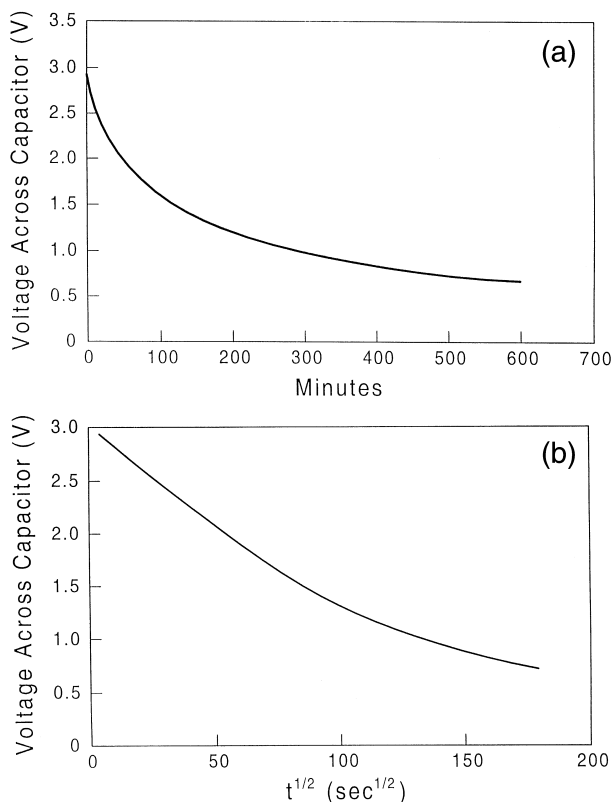


Fig. 3. Voltages during self-discharge of a 30 F supercapacitor calculated using the diffusion model. Curve (a) shows the time dependence of the voltage while curve (b) shows the dependence of the voltage on $t^{1/2}$.

considered. The exact nature of the electrochemical reactions which lead to excess ionic concentrations is not known but electrosorption of ions and redox reactions that involve surface-bonded ions would have to be considered [5]. There is some evidence that water contamination of an organic electrolyte can give rise to ionic species that accelerate the self-discharge of carbon-based capacitors [6].

For times less than h^2/D Eq. (7) can be simplified to:

$$V = V_0 - m\sqrt{t} \tag{8}$$

where the diffusion parameter m is given by:

$$m = \frac{c_{R0}\sqrt{D}}{C_{12}\sqrt{\pi}} \tag{9}$$

Taking q and C_{12} as fixed quantities for a given capacitor, m should depend only on c_{R0} and D . It is of interest to investigate how m varies with temperature and with the initial voltage of the capacitor. It should be noted that for supercapacitors made with the same carbon and the same electrolyte, the value of m should not depend significantly on the total area of the interfaces and, hence, on the total

capacitance. For such capacitors, m can be regarded as a measure of the excess ionic concentration c_{R0} which occurs in a particular capacitor.

3.1.1. Temperature dependence of diffusion rate

Since self-discharge rates are dependent on the rates of ionic transport, it is to be expected that self-discharge will become more rapid as the temperature of the capacitor is increased. Capacitor SCA272 was slowly charged to 2 V and the self-discharge rates were measured at 0°C, 20°C and 40°C. The self-discharge rate was fitted to a diffusion model for the first 500 min. As shown in Fig. 4, the diffusion parameter m increased strongly with increase in temperature while the leakage resistance R_{le} decreased. Since the capacitance is not strongly dependent on the temperature, it can be assumed from Eq. (9) that the temperature dependence of m comes mainly from the temperature dependence of the quantity $c_{R0}D^{1/2}$. $D^{1/2}$ cannot be expected to increase by more than 10% when the temperature is increased from 0°C to 40°C, so most of the increase in m must result from a strong dependence of c_{R0} on temperature. It appears, then, that an increase in the temperature of the capacitor accelerates the process leading to excess ionic concentrations near the electrodes of the capacitor.

3.1.2. Effect of the initial voltage on diffusion rate

The plots of V against $t^{1/2}$ shown in Fig. 5 are approximately linear over the first 8 h of self-discharge (for 8 h, $t^{1/2}$ is about 170 $s^{1/2}$) for the four initial voltages.

The data in Fig. 6 show that m increases strongly with increasing initial voltage above a threshold initial voltage of about 1 V. This dependence of m on the initial voltage arises from a strong dependence of the initial concentration

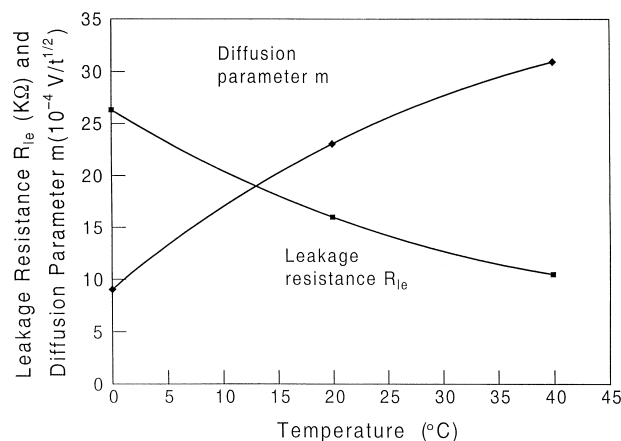


Fig. 4. Dependence of self-discharge mechanisms in capacitor SCA272 on temperature for an initial voltage of 2 V.

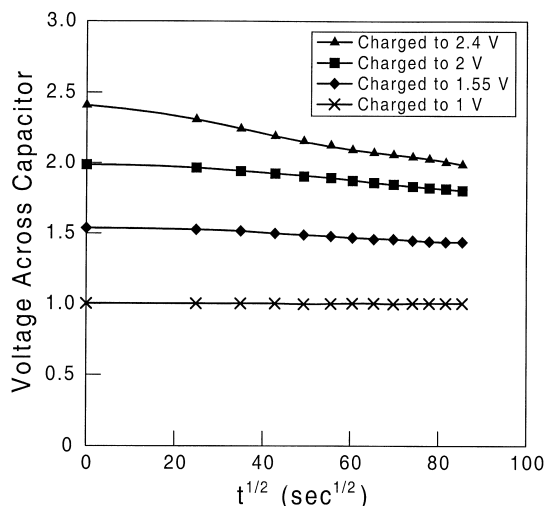


Fig. 5. Plots of the voltage against $t^{1/2}$ for capacitor SCA272 during 120 min of self-discharge from four initial voltages.

c_{R0} on the initial voltage. None of the other parameters on the right-hand side of Eq. (9) can be expected to show a significant dependence on V_0 . The process causing the accumulation of the ionic concentration near the electrodes appears to occur only when the capacitor is charged above 1 V.

3.1.3. Diffusion parameter in different capacitors

In the above sections of this paper, the diffusion mechanism has been illustrated by the self-discharge behaviour of capacitor SCA272. The self-discharge of several other capacitors was observed to see if SCA272 gave typical behaviour. The first several hours of the self-discharge of the eight capacitors listed in Table 1 followed the time dependence of the voltage decrease given by Eq. (8).

The values of the diffusion parameter in Table 1 do not have a large spread except for the high value for capacitor SCA245. The result for SCA245 may result from the use

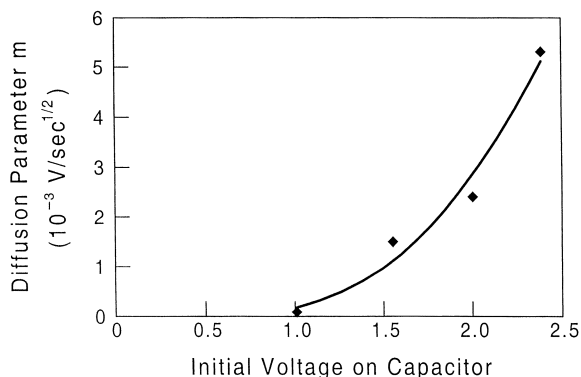


Fig. 6. Dependence of parameter m of diffusion model on initial voltage across capacitor SCA272.

of a type of activated carbon that was not used in any of the other capacitors in Table 1.

Capacitors produced more recently than those listed in Table 1 appear to have low values of m . Since methods of reducing the water content of the electrolyte have been progressively improved this lends support to the view that the presence of water enhances the processes that lead to excess ionic concentrations at the electrolyte–carbon interfaces of the capacitors.

3.2. Self-discharge through an ohmic leakage resistance

As stated in Section 1, if the dominant self-discharge mechanism is ohmic leakage through a resistance R_{le} the voltage will decay exponentially with a time constant of $R_{le}C$. The results given in Fig. 7 show that during self-discharge of capacitor SCA272, the voltage appears to decay exponentially after about 500 min. There is, however, a dependence of the effective leakage resistance on the initial voltage of the capacitor. For initial voltages of 1.55, 2.0 and 2.4 V, the effective time constants for the exponential decay are 125, 113 and 108 h, respectively. Since the capacitance (26 F) is approximately independent of voltage, these time constants correspond to equivalent leakage resistances of 17.4, 15.7 and 14.9 k Ω . This variation of the equivalent leakage resistance shows that the self-discharge rate for periods greater than 500 min after commencement of self-discharge cannot be modelled simply by discharge of the capacitor through a fixed leakage resistance.

A strong decrease in the equivalent leakage resistance as the temperature is increased is shown in Fig. 4. This is to be expected from the higher ionic mobilities that will increase the rate of leakage of charge across the double-layers as the temperature is increased.

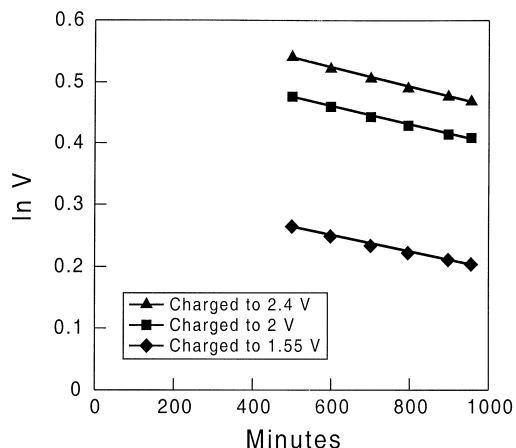


Fig. 7. Self-discharge of capacitor SCA272 showing that after about 500 min, the voltage V across the capacitor has an exponential decay rate.

4. Conclusions

In carbon-based supercapacitors with organic electrolytes, electrochemical reactions that can be modelled as a diffusion process cause significant loss of stored energy over a period of the order of 1 or 2 h. The nature of the reactions is not known, but it is probable that the presence of water in the organic electrolyte is a factor. The processes which lead to excess ionic concentration appear to occur only when a supercapacitor is charged to more than 1 V. When a supercapacitor is charged above 1 V, energy is stored by this mechanism in addition to energy stored by electrostatic charging of the double-layer of the capacitor. During the first 8 h of self-discharge, the energy stored by the ionic concentration mechanism is largely lost.

For times longer than 8 h, the voltage during self-discharge decays exponentially. There is some dependence of the self-discharge time constant on the initial voltage to which a capacitor is charged. This shows that the self-discharge rate for times greater than about 8 h cannot be simply represented by a constant leakage resistance in parallel with the capacitance of the double-layer at the electrolyte–carbon interface.

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